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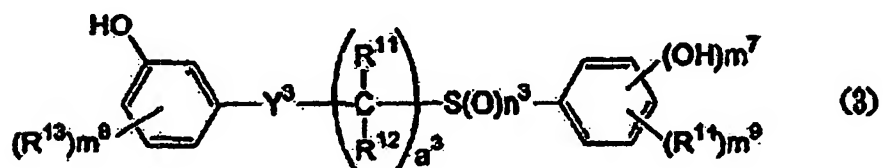
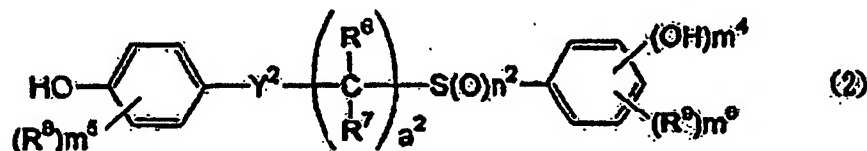
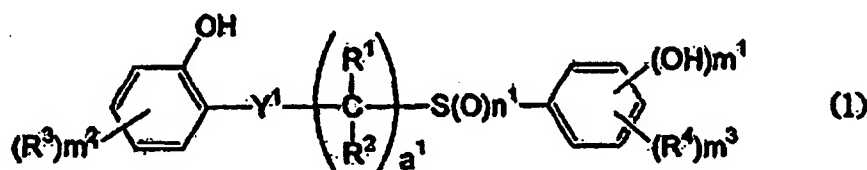
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(54) RECORDING MATERIAL AND RECORDING SHEET

(57)



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A recording material and a recording sheet free from surface fogging and excellent in dynamic coloring sensitivity, wet heat resistance, heat resistance, light resistance, plasticizer resistance, and water resistance. A recording material comprising a composition containing at least one kind of a compound (1) and at least one kind of a compound (2) and/or at least one kind a compound (3), and a recording sheet having a recording layer formed from the recording material. Compound (1) Compound (2) Compound (3) [in the formulae, R1, R2, R6, R7, R11, R12 indicate hydrogen atom or alkyl radical, a1-a3 integer of 1-6, n1-n3 0, 1 or 2, m1, m4 and m7 0, 1, 2, or 3. R3, R4, R8, R9 R13, R14 indicate alkyl radical or the like, m2, m3, m5, m6, m8 and m9 0, 1 or 2, Y1-Y3 Co or NRCO (R indicates hydrogen atom or the like)]

Description

TECHNICAL FIELD OF INVENTION

[0001] The present invention relates to a composition having an excellent dynamic sensitivity in recording as well as an excellent image stability and, particularly, having excellent resistance for heat and humidity, heat, light, plasticizer and water, relates to a recording material made from the composition and relates to a recording sheet comprising a base sheet and a recording material layer made from the recording material on the base sheet.

BACKGROUND ART

[0002] A recording material making use of color development based on a chemical reaction between a color forming dye and a developer is capable of carrying out a recording process in a relatively simple apparatus and within a short period of time without performing complicated processing such as development fixing. Thus, such recording material is used in a wide range of applications including pressuresensitive copying materials or thermal recording materials of output-recording units employed in facsimile machines or printers.

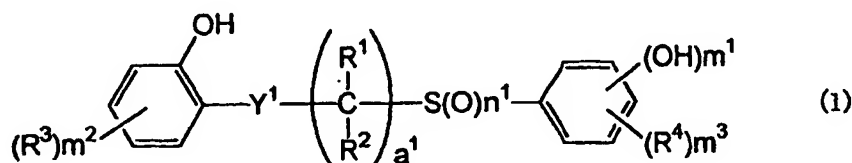
[0003] The capability to develop colors quickly and maintain the whiteness of the portion with no developed colors is demanded of these recording materials. The portion with no developed colors is hereafter referred to as the background. In addition, high durability of background and image is demanded of these recording materials. In recent years, particularly, a large amount of recording material is being used in a field where the reliability of a recorded image is considered to be of high importance. As a result, there is an increase in the demand for a recording material having an excellent image stability such as heat and humidity, heat, light, water and plasticizer (included in a macromolecular material) resistance.

[0004] With one kind of developer, however, it is difficult to provide a recording material satisfying all the demands described above. In addition, while attempts have been made to use a mixture consisting of a developer exhibiting a good heat and humidity resistance and a developer having a good light resistance, a recording material that sufficiently satisfies all the requirements has not yet been invented. As described earlier, the requirements include an excellent sensitivity in recording, heat and humidity, heat, light, plasticizer and water resistance. When a recording material does not satisfy all the requirements, a phenomenon called background fogging typically occurs after the creation of a piece of thermal recording paper. A background fogging is a phenomenon in which color is generated on the thermal recording paper.

DISCLOSURE OF THE INVENTION

[0005] In accordance with a first aspect of the present invention, there is provided a composition including:

at least one type of a compound represented by Formula (1); wherein



R¹ and R² each independently represent hydrogen or C1 - C6 alkyl,

a¹ represents an integer of 1 to 6,

n¹ represents 0, 1 or 2,

m¹ represents 0 or an integer in the range 1 to 3,

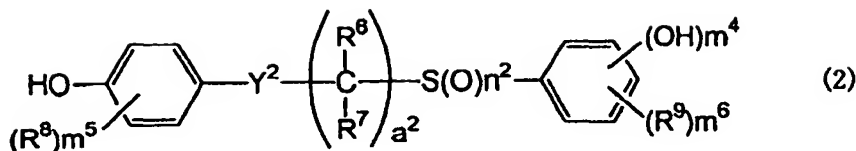
R³ and R⁴ each independently represent nitro, carboxyl, halogen, C1-C6 alkyl or C2-C6 alkenyl,

m² and m³ each independently represent 0, 1 or 2;

R³ and R⁴ may be different to each other when m² and m³ represent each 2,

Y¹ represents CO or NR⁵CO (in the equation, R⁵ represents hydrogen or C1-C6 alkyl);

at least one type of a compound represented by Formula (2); wherein



R⁶ and R⁷ each independently represent hydrogen or C1 - C6 alkyl,

a² represents an integer of 1 to 6,

n² represents 0, 1 or 2,

m⁴ represents 0 or an integer in the range 1 to 3,

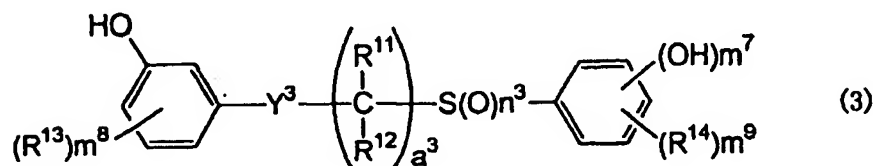
R⁸ and R⁹ each independently represent nitro, carboxyl, halogen, C1-C6 alkyl or C2-C6 alkenyl,

m⁵ and m⁶ each independently represent 0, 1 or 2;

R⁸ and R⁹ may be different to each other when m⁵ and m⁶ represent each 2,

Y² represents CO or NR¹⁰CO (in the equation, R¹⁰ represents hydrogen or C1-C6 alkyl); and/or

at least one type of a compound represented by Formula (3); wherein



R¹¹ and R¹² each independently represent hydrogen or C1 - C6 alkyl,

a³ represents an integer of 1 to 6,

n³ represents 0, 1 or 2,

m⁷ represents 0 or an integer in the range 1 to 3,

R¹³ and R¹⁴ each independently represent nitro, carboxyl, halogen, C1-C6 alkyl or C2-C6 alkenyl,

m⁸ and m⁹ each independently represent 0, 1 or 2;

R¹³ and R¹⁴ may be different to each other when m⁸ and m⁹ represent each 2,

Y³ represents CO or NR¹⁵CO (in the equation, R¹⁵ represents hydrogen or C1-C6 alkyl);

[0006] In accordance with a second aspect of the present invention, there is provided a recording material including at least one type of the compound represented by the said Formula (1), at least one type of the compound represented by the said Formula (2) and/or at least one type of the compound represented by the said Formula (3).

[0007] It is desirable to provide the recording material according to the second aspect of the present invention wherein the compound represented by the said Formula (2) and/or the compound represented by the said Formula (3) each have a content quantity in the range 5 to 500 parts by weight relative to 100 parts by weight of the compound represented by the said Formula (1).

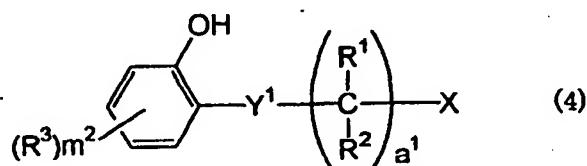
[0008] In accordance with a third aspect of the present invention, there is provided a recording sheet comprising a base sheet and a recording material layer made from the recording material according to the second aspect of the present invention on the said base sheet.

[0009] The recording material layer made from the recording material according to the second aspect of the present invention has an excellent dynamic sensitivity in recording as well as an excellent image stability and, particularly, has excellent property such as heat and humidity, heat, light, plasticizer and water resistance. In addition, there is no generation of the background fogging phenomenon, which is commonly observed in conventional methods that use a mixture of the developers. In the present invention, dynamic sensitivity is defined as a sensitivity obtained as a optical density measured by instantaneously applying thermal energy generated by a thermal head (employed in a thermal printer) in the form of an ordinary pulse having a duration in the range 0.2 to 1.8 msec to a piece of thermal recording paper.

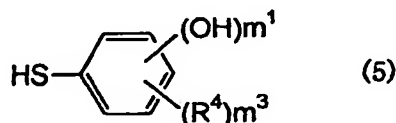
[0010] As described above, the composition provided by the present invention comprises at least one type of the compound represented by the said Formula (1), at least one type of the compound represented by the said Formula (2) and/or at least one type of the compound represented by the said Formula (3). While the weight ratios among the

compounds are arbitrary, the compound represented by the said Formula (2) and/or the compound represented by the said Formula (3) normally each have a content quantity in the range 5 to 500 parts by weight relative to 100 parts by weight of the compound represented by the said Formula (1). It is desirable, however, to adjust the weight ratios so that the compound represented by the said Formula (2) and/or the compound represented by the said Formula (3) each have a content quantity in the range 10 to 300 parts by weight relative to 100 parts by weight of the compound represented by the said Formula (1). It is even more desirable to adjust the weight ratios so that the compound represented by the said Formula (2) and/or the compound represented by the said Formula (3) each have a content quantity in the range 20 to 250 parts by weight relative to 100 parts by weight of the compound represented by the said Formula (1).

[0011] The compounds represented by the said Formula (1), wherein the portion of $S(O)n^1$ is S, to be used in the present invention can be obtained by the reaction of the compound represented by Formula (4);



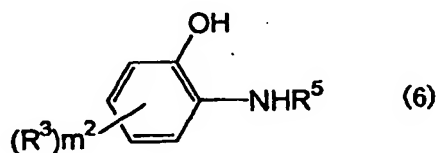
wherein R^1 , R^2 , R^3 , Y^1 , a^1 and m^2 each have the same meaning as the one previously described, and X represents halogen, such as a chlorine or bromine, with a compound represented by Formula (5);



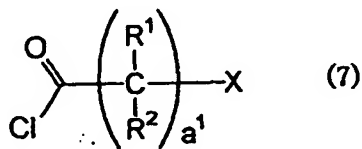
wherein R^4 , m^1 and m^3 each have the same meaning as the one previously described, in an organic solvent such as methanol with the presence of a base such as a potassium hydroxide.

[0012] Compounds represented by the said Formula (1), wherein the portion of $S(O)n^1$ is SO or SO_2 , may be obtained by oxidizing the compound obtained by the reaction herein above with an oxidizing agent, such as aqueous solution of hydrogen peroxide and m-chloroperbenzoic acid in an organic solvent such as acetic acid

[0013] Compounds represented by the said Formula (4), wherein the portion of Y^1 is NR^5CO , can be obtained by the reaction of the compound represented by Formula (6);

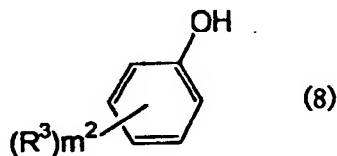


wherein R^3 , R^5 and m^2 each have the same meaning as the one previously described, with the compound represented by Formula (7);



wherein R^1 , R^2 , X and a^1 each have the same meaning as the one previously described, in an organic solvent such as acetonitrile, and water with the presence of a base such as potassium bicarbonate.

[0014] Compounds represented by the said Formula (4), wherein the portion of Y is CO, can be obtained by the reaction of the compound represented by Formula (8);



wherein R^3 and m^2 each have the same meaning as the one previously described, with a compound represented by the said Formula (7), in an organic solvent such as dichloromethane with the presence of a Lewis acid such as aluminum chloride.

[0015] A compound represented by the said Formula (2) and a compound represented by the said Formula (3) can each be synthesized in the same way as a compound represented by the said Formula (1).

[0016] As methods of mixing a compound represented by Formula (1) with a compound(s) represented by Formulas (2) and/or (3), it is possible to adopt a method of mixing powders of the compounds, a fusion-mixing method, a method of adding and mixing of the compounds during crystallization of the compound represented by Formula (1) and a method of having a chemical reaction using a mixture such as o-hydroxyaniline, m-hydroxyaniline or p-hydroxyaniline as hydroxyaniline of the raw materials and synthesizing/including compounds of at least two or three types at the same time.

[0017] In Formula (1), R^1 and R^2 each independently represent hydrogen; C1 - C6 alkyl such as methyl, ethyl, n-propyl, isopropyl, n-butyl and tert-butyl.

a^1 represents an integer of 1 to 6;

n^1 represents 0, 1 or 2;

m^1 represents 0 or an integer of 1 to 3.

[0018] R^3 and R^4 each independently represent nitro; carboxyl; halogen such as fluorine, chlorine, bromine and iodine; C1 - C6 alkyl such as methyl, ethyl, n-propyl, isopropyl, n-butyl and tert-butyl; C2 - C6 alkenyl such as propenyl, isopropenyl and butenyl.

m^2 and m^3 each independently represent 0, 1 or 2, and

Y^1 represents CO or NR^5CO .

R^5 represents hydrogen; C1 - C6 alkyl such as methyl, ethyl, n-propyl, isopropyl, n-butyl and tert-butyl.

[0019] Compounds represented by Formula (1) particularly include a preferred compound in which Y^1 represents NR^5CO and a more preferred compound in which Y^1 represents $NHCO$.

Examples of compounds represented by Formula (1) are N-(2'-hydroxyphenylthio) acetyl-2-hydroxyaniline, N-(3'-hydroxyphenylthio)acetyl-2-hydroxyaniline, N-(4'-hydroxyphenylthio)acetyl-2-hydroxyaniline and the like.

[0020] Another recording material provided by the present invention includes at least one type of the compound represented by Formula (2) and at least one type of the compound represented by Formula (3).

[0021] In Formula (2), R^6 and R^7 each independently represent hydrogen; C1 - C6 alkyl such as methyl, ethyl, n-propyl, isopropyl, n-butyl and tert-butyl.

a^2 represents an integer of 1 to 6, and

n^2 represents 0, 1 or 2.

m^4 represents 0 or an integer of 1 to 3.

[0022] R^8 and R^9 each independently represent nitro; carboxyl; halogen such as fluorine, chlorine, bromine and iodine; C1 - C6 alkyl such as methyl, ethyl, n-propyl, isopropyl, n-butyl and tert-butyl; C2 - C6 alkenyl such as propenyl, isopropenyl and butenyl.

m^5 and m^6 each independently represent 0, 1 or 2, and

Y^2 represents CO or $NR^{10}CO$.

R^{10} represents hydrogen; C1 - C6 alkyl, such as methyl, ethyl, n-propyl, isopropyl, n-butyl and tert-butyl.

[0023] Compounds represented by Formula (2) particularly include a preferred compound in which Y^2 represents $NR^{10}CO$ and a more preferred compound in which Y^2 represents $NHCO$.

[0024] Examples of the compounds represented by Formula (2) are the N-(2'-hydroxy phenyl thio) acetyl-4-hydroxy aniline, the N-(3'-hydroxy phenyl thio) acetyl-4-hydroxy aniline, the N-(4'-hydroxy phenyl thio) acetyl-4-hydroxy aniline and the like.

[0025] In Formula (3), R¹¹ and R¹² each independently represent hydrogen; C1 - C6 alkyl such as methyl, ethyl, n-propyl, isopropyl, n-butyl and tert-butyl.

a³ represents an integer of 1 to 6, and

n³ represents 0, 1 or 2, and

m⁷ represents 0 or an integer of 1 to 3.

[0026] R¹³ and R¹⁴ each independently represent nitro; carboxyl; halogen such as fluorine, chlorine, bromine and iodine; C1 - C6 alkyl such as methyl, ethyl, n-propyl, isopropyl, n-butyl and tert-butyl; C2 - C6 alkenyl such as propenyl, isopropenyl and butenyl.

m⁸ and m⁹ each independently represent 0, 1 or 2, and

Y³ represents CO or NR¹⁵CO.

R¹⁵ represents hydrogen; C1 - C6 alkyl such as methyl, ethyl, n-propyl, isopropyl, n-butyl and tert-butyl.

[0027] Compounds represented by Formula (3) particularly include a preferred compound in which Y³ represents NR¹⁵CO and a more preferred compound in which Y³ represents NHCO.

[0028] Examples of the compounds represented by Formula (3) are the N-(2'-hydroxy phenyl thio) acetyl-3-hydroxy aniline, the N-(3'-hydroxy phenyl thio) acetyl-3-hydroxy aniline, the N-(4'-hydroxy phenyl thio) acetyl-3-hydroxy aniline and the like.

[0029] Preferred examples of the composition comprising a compound represented by the said Formula (1) and a compound represented by the said Formula (2) and/or (3) are items (a) to (c) listed as follows.

(a) N-(4'-hydroxyphenylthio)acetyl-2-hydroxyaniline and N-(4'-hydroxyphenylthio)acetyl-4-hydroxyaniline.

(b) N-(4'-hydroxyphenylthio)acetyl-2-hydroxyaniline and N-(4'-hydroxyphenylthio)acetyl-3-hydroxyaniline.

(c) N-(4'-hydroxyphenylthio)acetyl-2-hydroxyaniline, N-(4'-hydroxyphenylthio)acetyl-4-hydroxyaniline and N-(4'-hydroxyphenylthio)acetyl-3-hydroxyaniline.

[0030] The recording material provided by the present invention includes at least one type of a color forming dye and a compound represented by the said Formula (1) in addition to compounds represented by the said Formula (2) and/or Formula (3). That is to say, the recording material provided by the present invention may include both compounds represented by the said Formula (2) and Formula (3) or include only a compound represented by either the said Formula (2) or Formula (3).

[0031] In the recording material provided by the present invention, the compound represented by Formula (1) normally has a content quantity in the range 10 to 500 parts by weight relative to 100 parts by weight of the color forming dye. It is desirable, however, to adjust the weight ratio so that the compound represented by Formula (1) has a content quantity in the range 50 to 300 parts by weight relative to 100 parts by weight of the color forming dye. It is even more desirable to adjust the weight ratio so that the compound represented by Formula (1) has a content quantity in the range 50 to 200 parts by weight relative to 100 parts by weight of the color forming dye. If the compound represented by Formula (1) has a relative content quantity of 10 parts by weight or smaller, a sufficient saturated density will not be achieved. If the compound represented by Formula (1) has a relative content quantity greater than 500 parts by weight, on the other hand, the general content quantity of the developer is considered to be excessively large even though there is no conceivable bad effect in particular. An excessively large content quantity is not desirable because such a content quantity raises the cost of the thermal recording paper.

[0032] In addition, the compound represented by Formula (2) and the compound represented by Formula (3) normally have a total content quantity in the range 5 to 500 parts by weight relative to 100 parts by weight of the compound represented by Formula (1). It is desirable, however, to adjust the weight ratios so that the compound represented by Formula (2) and the compound represented by Formula (3) have a total content quantity in the range 10 to 300 parts by weight relative to 100 parts by weight of the compound represented by Formula (1). It is even more desirable to adjust the weight ratios so that the compound represented by Formula (2) and the compound represented by Formula (3) have a total content quantity in the range 20 to 250 parts by weight relative to 100 parts by weight of the compound represented by Formula (1). If the compound represented by Formula (2) and the compound represented by Formula (3) have a total relative content quantity of 5 parts by weight or smaller, it is feared that the heat and humidity resistance and plasticizer resistance of the image will deteriorate. If the compound represented by Formula (2) and the compound represented by Formula (3) have a total relative content quantity greater than 500 parts by weight, on the other hand, it is feared that the light resistance of the image will deteriorate.

[0033] In addition, the compound represented by Formula (1) and the compound represented by Formula (2) and/or the compound represented by Formula (3) normally have a total content quantity in the range 100 to 1,000 parts by weight relative to 100 parts by weight of the color forming dye. It is desirable, however, to adjust the weight ratios so that the compound represented by Formula (1) and the compound represented by Formula (2) and/or the compound represented by Formula (3) normally have a total content quantity in the range 150 to 500 parts by weight relative to 100 parts by weight of the color forming dye.

[0034] The composition and recording material of the present invention may include same compounds of a different degree of crystallinity as well as a variable crystalline form, those in an amorphous state and an adduct of the solvent. By properly selecting and using compounds with different crystalline forms, the background and sensitivity of the recording material can probably be improved. In addition, if the particle diameter of the compounds in a coating solution is made smaller, the sensitivity may be improved. In particular, the substance having a high degree of crystallinity results in a background with excellent brightness and an excellent heat resistance in comparison with a substance put in an amorphous state.

[0035] Methods of mixing the compound represented by the said Formula (1) and the compound represented by the said Formula (2) and/or the compound represented by the said Formula (3) include a method of mixing particles of the compounds, an additive method implemented during liquid mixture adjustment/dispersion time and an additive method implemented in a state of an dispersion. In addition, by selecting a process to produce compounds, a mixture of the compound represented by the said Formula (1) and the compound represented by the said Formula (2) and/or the compound represented by the said Formula (3) can be obtained in the process and used as it is.

[0036] The recording material of the present invention may also contain one or more of a known developer, an image stabilizer, an antioxidant, a desensitizer, an antitack agent, an antifoamer, a photo stabilizer and a fluorescent dye. These additional agents may be contained either in the color forming layer, or in an arbitrary layer, for example a protecting layer when the recording material is configured by a multi-layer structure. In particular, in the case of a structure including an overcoat layer and an undercoat layer respectively over and under the color forming layer, an antioxidant and a photo stabilizer may be included in the overcoat and undercoat layers by being contained in micro-capsules if necessary.

[0037] Examples of the color forming dye used for the recording material of the present invention include leuco dyes based on fluoran, phthalide, lactam, triphenyl methane, phenothiazine, and spiropyran. However, the color forming dyes are not limited to these leuco dyes, and any color forming dyes may be used as far as it forms color by contacting with a developer of an acidic substance.

[0038] Examples of the color forming dyes based on fluoran include 3-diethylamino-6-methyl-7-anilino fluoran, 3-dibutylamino-6-methyl-7-anilino fluoran, 3-(N-ethyl-N-isobutylamino)-6-methyl-7-anilino fluoran, 3-(N-methyl-N-propylamino)-6-methyl-7-anilino fluoran, 3-(N-ethyl-N-isopentylamino)-6-methyl-7-anilino fluoran, 3-diethylamino-7-(o-chloroanilino)fluoran, 3-dibutylamino-7-(o-chloroanilino) fluoran, 3-(N-ethyl-p-toluidino)-6-methyl-7-anilino fluoran, 3-(N-cyclohexyl-N-methylamino)-6-methyl-7-anilino fluoran, 3-pyrrolidino-6-methyl-7-anilino fluoran, 3-piperidino-6-methyl-7-anilino fluoran, 3-dimethylamino-7-(m-trifluoromethylanilino)fluoran, 3-dipentylamino-6-methyl-7-anilino fluoran, 3-(N-ethoxypropyl-N-ethylamino)-6-methyl-7-anilino fluoran, 3-dibutylamino-7-(o-fluoroanilino)fluoran, 3-diethylaminobenzo[a]fluoran, 3-dimethylamino-6-methyl-7-chlorofluoran, 3-diethylamino-5-methyl-7-dibenzylaminofluoran, 3-diethylamino-7-dibenzylaminofluoran, 3-diethylamino-5-chlorofluoran, 3-diethylamino-6-(N, N-dibenzylamino)fluoran, 3,6-dimethoxyfluoran, and 2, 4-dimethyl-6-(4-dimethylaminophenyl)aminofluoran.

[0039] Examples of the color forming dyes based on phthalide include 3-{4-[4-(4-anilino)-anilino]anilino}-6-methyl-7-chlorofluoran,

3,3-bis[2-(4-dimethylaminophenyl)-2-(4-methoxyphenyl)vinyl]-4,5,6,7-tetrachlorophthalide, 3,6,6'-tris(dimethylamino)spiro(fluorine-9,3'-phthalide), and 3,3-bis(4'-diethylaminophenyl)-6-diethylaminophthalide.

[0040] In particular, it is desirable to use color forming dyes pertaining to fluoran such as 3-diethylamino-6-methyl-7-anilino fluoran,

3-dibutylamino-6-methyl-7-anilino fluoran, 3-(N-ethyl-N-isobutylamino)-6-methyl-7-anilino fluoran, 3-(N-methyl-N-propylamino)-6-methyl-7-anilino fluoran, 3-(N-ethyl-N-isopentylamino)-6-methyl-7-anilino fluoran,

3-diethylamino-7-(o-chloroanilino)fluoran,
 3-dibutylamino-7-(o-chloroanilino)fluoran,
 3-(N-ethyl-p-toluidino)-6-methyl-7-anilinofluoran,
 3-(N-cyclohexyl-N-methylamino)-6-methyl-7-anilinofluoran,
 5 3-pyrrolidino-6-methyl-7-anilinofluoran,
 3-piperidino-6-methyl-7-anilinofluoran,
 3-dimethylamino-7-(m-trifluoromethylanilino)fluoran,
 3-dipentylamino-6-methyl-7-anilinofluoran,
 3-(N-ethoxypropyl-N-ethylamino)-6-methyl-7-anilinofluoran,
 10 3-dibutylamino-7-(o-fluoroanilino)fluoran,
 3-diethylbenzo[a]fluoran,
 3-dimethylamino-6-methyl-7-chlorofluoran,
 3-diethylamino-5-methyl-7-dibenzylaminofluoran,
 3-diethylamino-7-dibenzylaminofluoran,
 15 3-diethylamino-5-chlorofluoran,
 3-diethylamino-6-(N,N'-dibenzylamino)fluoran,
 3,6-dimethoxyfluoran and 2,4-dimethyl-6-(4-dimethylaminophenyl)aminofluoran.

[0041] It is even more desirable to use color forming dyes pertaining to fluoran such as 3-diethylamino-6-methyl-7-anilinofluoran,

20 3-dibutylamino-6-methyl-7-anilinofluoran,
 3-(N-ethyl-N-isobutylamino)-6-methyl-7-anilinofluoran,
 3-(N-methyl-N-propylamino)-6-methyl-7-anilinofluoran,
 3-(N-ethyl-N-isopentylamino)-6-methyl-7-anilinofluoran and 3-(N-cyclohexyl-N-methylamino)-6-methyl-7-anilinofluoran.

25 [0042] Of course, these color forming dyes can each be used alone to give a recording material of a color developed by the dye, or two or more types of color forming dye can be mixed with each other. For example, it is possible to mix the color forming dyes of the elementary colors, namely, red, green and blue, or a black dye to make a recording material develop the truly black color.

Other developers include those for thermal recording materials and those for pressuresensitive recording materials.

30 Examples for the developer of thermal recording materials include bisphenol compounds, such as bisphenol A,

4,4'-sec-butylidenbisphenol,

4,4'-cyclohexylidenbisphenol,

2,2-dimethyl-3,3-bis(4-hydroxyphenyl)butane,

2,2'-dihydroxydiphenyl,

35 pentamethylene-bis(4-hydroxybenzoate),

2,2-dimethyl-3,3-di(4-hydroxyphenyl)pentane,

2,2-di(4-hydroxyphenyl)hexane;

sulfur-containing bisphenol compounds, such as 4,4'-dihydroxydiphenylthio ether, 1,7-di(4-hydroxyphenylthio)-3,5-dioxaheptane,

40 2,2'-bis(4-hydroxyphenylthio)diethyl ether,

4,4'-dihydroxy-3,3'-dimethyldiphenylthio ether;

4-hydroxybenzoic esters, such as benzyl 4-hydroxybenzoate,

ethyl 4-hydroxybenzoate,

propyl 4-hydroxybenzoate,

45 isopropyl 4-hydroxybenzoate,

butyl 4-hydroxybenzoate,

isobutyl 4-hydroxybenzoate,

chlorobenzyl 4-hydroxybenzoate,

methylbenzyl 4-hydroxybenzoate and diphenylmethyl 4-hydroxybenzoate;

50 metal salts of benzoic acid, such as zinc benzoate and zinc 4-nitrobenzoate;

salicylic acids, such as 4-[2-(4-methoxyphenoxy)ethoxy]salicylic acid;

metal salts of salicylic acid, such as zinc salicylate and bis[4-(octyloxycarbonylamino)-2-hydroxybenzoic acid] zinc;

hydroxysulfones, such as

4,4'-dihydroxydiphenylsulfone,

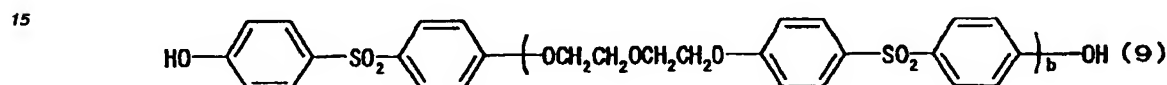
55 2,4'-dihydroxydiphenylsulfone,

4-hydroxy-4'-methyldiphenylsulfone,

4-hydroxy-4'-isopropoxydiphenylsulfone,

4-hydroxy-4'-butoxydiphenylsulfone,

4,4'-dihydroxy-3,3'-diallyldiphenylsulfone,
 3,4-dihydroxy-4'-methyldiphenylsulfone,
 4,4'-dihydroxy-3,3',5,5'-tetrabromodiphenylsulfone;
 4-hydroxyphthalic diesters, such as dimethyl 4-hydroxyphthalate,
 5 dicyclohexyl 4-hydroxyphthalate and diphenyl 4-hydroxyphthalate;
 hydroxynaphthoic esters, such as 2-hydroxy-6-carboxynaphthalene;
 trihalomethylsulfones, such as tribromomethylphenylsulfone;
 sulfonylureas, such as 4,4'-bis(p-toluenesulfonylamino)carbonylamino)diphenylmethane;
 tetracyanoquinodimethanes; hydroxyacetophenone; p-phenylphenol;
 10 benzyl 4-hydroxyphenylacetate; p-benzylphenol; hydroquinonemonobenzyl ether; 2,4-dihydroxy-2'-methoxydiben-
 zanilide; and
 diphenylsulfone bridged compounds represented by Formula (9) given below;



20 wherein b is an integer of 0 to 6, and mixtures of the compounds described above
[0043] And examples of the developer for pressure-sensitive recording materials are:

inorganic acids, such as acid clay,
 activated clay,
 25 attapulgite,
 bentonite,
 colloidal silica,
 aluminum silicate,
 magnesium silicate,
 30 zinc silicate,
 tin silicate,
 burned kaolin and talc;
 aliphatic carboxylic acids, such as oxalic acid,
 maleic acid,
 35 tartaric acid,
 citric acid,
 succinic acid, and stearic acid;
 aromatic carboxylic acids, such as benzoic acid,
 p-t-butyl benzoate,
 40 phthalic acid,
 gallic acid,
 salicylic acid, such as 3-isopropyl salicylate,
 3-phenyl salicylate,
 3-cyclohexyl salicylate,
 45 3,5-di-t-butyl salicylate,
 3-methyl-5-benzyl salicylate,
 3-phenyl-5-(2,2-dimethylbenzyl)salicylate,
 3,5-di-(2-methylbenzyl)salicylate and 2-hydroxy-1-benzyl-3-naphthate;
 salts derived from these aromatic carboxylic acids through displacement by such metals as zinc, magnesium,
 50 aluminum and titanium;
 developers of phenolic resin, such as p-phenylphenol-formalin resin and p-butylphenol-acetylene resin, and
 mixtures of these developers of phenolic resin and the metal salts of aromatic carboxylic acids described above.

[0044] Examples for the image stabilizer include
 55 epoxycontaining diphenylsulfones, such as 4-benzoyloxy-4'-(2-methylglycidyloxy)-diphenylsulfone, and 4,4'-diglycidy-
 loxydiphenylsulfone; and
 1,4-diglycidyloxybenzene;
 4-[α-(hydroxymethyl)benzyloxy]-4'-hydroxydiphenylsulfone;

2-propanol derivative;
 salicylic acid derivative;
 metal salts of oxynaphthoic acid derivatives (particular, zinc salt);
 metal salts of 2,2-methylenebis(4,6-t-butylphenyl)phosphate and other water-insoluble zinc-containing compounds.

5 [0045] Examples for the sensitizer include

higher fatty acid amides, such as the stearic amide;

benzamides;

anilide, such as stearic anilide, acetoacetic anilide and thioacetoanilide;

dibenzyl oxalate, di(4-methylbenzyl) oxalate, di(4-chlorobenzyl) oxalate, dimethyl phthalate, dimethyl terephthalate,

10 dibenzyl terephthalate, dibenzyl isophthalate,

and kinds of bis(t-butylphenol)s;

diphenylsulfone and its derivatives;

diethers of 4,4'-dihydroxydiphenylsulfone, such as 4,4'-dimethoxydiphenylsulfone, 4,4'-diethoxydiphenylsulfone,

4,4'-dipropoxydiphenylsulfone,

15 4,4'-diisopropoxydiphenylsulfone,

4,4'-dibutoxydiphenylsulfone,

4,4'-diisobutoxydiphenylsulfone,

4,4'-dipentyloxydiphenylsulfone and the 4,4'-dihexyloxydiphenylsulfone;

diethers of 2,4-dihydroxydiphenylsulfone, such as 2,4'-dimethoxydiphenylsulfone, 2,4'-diethoxydiphenylsulfone,

20 2,4'-dipropoxydiphenylsulfone,

2,4'-diisopropoxydiphenylsulfone,

2,4'-dibutoxydiphenylsulfone,

2,4'-diisobutoxydiphenylsulfone,

2,4'-dipentyloxydiphenylsulfone and 2,4'-dihexyloxydiphenylsulfone; and

25 1,2-bis(phenoxy)ethane,

1,2-bis(4-methylphenoxy)ethane,

1,2-bis(3-methylphenoxy)ethane,

2-naphtholbenzyl ether,

diphenyl amine,

30 carbazole,

2,3-di-m-tolylbutane,

4-benzylbiphenyl,

4,4'-dimethylbiphenyl,

m-triphenyl,

35 di-β-naphthylphenylene diamine,

phenyl 1-hydroxynaphthoate,

2-naphthylbenzyl ether,

4-methylphenyl-biphenyl ether,

2,2-bis(3,4-dimethylphenyl)ethane,

40 2,3,5,6-tetramethyl-4'-methylidiphenylmethane and diphenyl carboxylate.

[0046] In particular, desirable sensitizers include;

Ethers, such as 1,2-bis(phenoxy)ethane,

1,2-bis(3-methylphenoxy)ethane and 2-naphthylbenzyl ether,

aromatic hydrocarbons, such as m-terphenyl,

45 4-benzylbiphenyl and di(4-methylbenzyl)oxalate;

diphenylsulfone and derivatives of diphenylsulfone;

diethers of 4,4'-dihydroxydiphenylsulfone; and

diethers of 2,4'-dihydroxydiphenylsulfone.

[0047] As the filler, silica, clay, kaolin, burned kaolin, talc, satin white, aluminum hydroxide, calcium carbonate, magnesium carbonate, zinc oxide, titanium oxide, barium sulfate, magnesium silicate, aluminum silicate, plastic pigment and the like may be used. In the recording material of the present invention, salts of alkaline earth metals are particularly preferable, and carbonates, such as calcium carbonate and magnesium carbonate are further preferable.

[0048] Examples for the dispersing agent include sulfosuccinic esters, such as dioctylsodium sulfosuccinate,

sodium dodecylbenzene sulfonate,

55 and sodium salt and fatty acid salt of lauryl alcohol sulfuric ester.

[0049] Examples for the antioxidant include 2,2'-methylenebis(4-methyl-6-t-butylphenol),

2,2'-methylenebis(4-ethyl-6-t-butylphenol),

4,4'-propylmethylenebis(3-methyl-6-t-butylphenol),

4,4'-butylidenebis(3-methyl-6-*t*-butylphenol),
 4,4'-thiobis(2-*t*-butyl-5-methylphenol),
 1,1,3-tris(2-methyl-4-hydroxy-5-*t*-butylphenyl)butane,
 1,1,3-tris(2-methyl-4-hydroxy-5-cyclohexylphenyl)butane and 4-[4-[1,1-bis(4-hydroxyphenyl)ethyl]- α,α -dimethylbenzyl]phenol.

[0050] As the desensitizer, aliphatic higher alcohols, polyethylene glycol, and guanidine derivatives and the like may be used.

[0051] Examples for the antitack agent include stearic acid, zinc stearate, calcium stearate, carnauba wax, paraffin wax and ester wax.

[0052] Examples for the photostabilizing agent include salicylic acid based ultraviolet radiation absorbents, such as phenyl salicylate, *p*-*t*-butylphenyl salicylate and *p*-octylphenyl salicylate;

[0053] Benzophenone based ultraviolet radiation absorbents, such as the 2,4-dihydroxybenzophenone, 2-hydroxy-4-methoxybenzophenone,

2-hydroxy-4-benzoyloxybenzophenone,

2-hydroxy-4-octyloxybenzophenone,

2-hydroxy-4-dodecyloxybenzophenone,

2,2'-dihydroxy-4-methoxybenzophenone,

2,2'-dihydroxy-4,4'-dimethoxybenzophenone,

2-dihydroxy-4-methoxy-5-sulfolbenzophenone and bis(2-methoxy-4-hydroxy-5-benzoylphenyl)methane; and

[0054] benzotriazole based ultraviolet radiation absorbents, such as 2-(2'-hydroxy-5'-methylphenyl)benzotriazole,

2-(2'-hydroxy-5'-*t*-butylphenyl)benzotriazole,

2-(2'-hydroxy-3',5'-di-*t*-butylphenyl)benzotriazole,

2-(2'-hydroxy-3'-*t*-butyl-5'-methylphenyl)-5-chlorobenzotriazole, 2-(2'-hydroxy-3',5'-di-*t*-butylphenyl)-5-chlorobenzotriazole,

2-(2'-hydroxy-3',5'-di-*t*-amylphenyl)benzotriazole, 2-[2'-hydroxy-3'-(3",4",5",6"-tetrahydrophthalimidemethyl)-5'-*t*-methylphenyl]benzotriazole, 2-(2'-hydroxy-5'-*t*-octylphenyl)benzotriazole,

2-[2'-hydroxy-3',5'-bis(α,α -dimethylbenzyl)phenyl]-2H-benzotriazole, 2-(2'-hydroxy-3'-dodecyl-5'-methylphenyl)benzotriazole,

2-(2'-hydroxy-3'-undecyl-5'-methylphenyl)benzotriazole,

2-(2'-hydroxy-3'-tridecyl-5'-methylphenyl)benzotriazole,

2-(2'-hydroxy-3'-tetradecyl-5'-methylphenyl)benzotriazole,

2-(2'-hydroxy-3'-pentadecyl-5'-methylphenyl)benzotriazole,

2-(2'-hydroxy-3'-hexadecyl-5'-methylphenyl)benzotriazole,

2-[2'-hydroxy-4'-(2"-ethylhexyl)oxyphenyl]benzotriazole,

2-[2'-hydroxy-4'-(2"-ethylheptyl)oxyphenyl]benzotriazole,

2-[2'-hydroxy-4'-(2"-ethyloctyl)oxyphenyl]benzotriazole,

2-[2'-hydroxy-4'-(2"-propyloctyl)oxyphenyl]benzotriazole,

2-[2'-hydroxy-4'-(2"-propylheptyl)oxyphenyl]benzotriazole,

2-[2'-hydroxy-4'-(2"-propylhexyl)oxyphenyl]benzotriazole,

2-[2'-hydroxy-4'-(1"-ethylhexyl)oxyphenyl]benzotriazole,

2-[2'-hydroxy-4'-(1"-ethylheptyl)oxyphenyl]benzotriazole,

2-[2'-hydroxy-4'-(1"-ethyloctyl)oxyphenyl]benzotriazole,

2-[2'-hydroxy-4'-(1"-propyloctyl)oxyphenyl]benzotriazole,

2-[2'-hydroxy-4'-(1"-propylheptyl)oxyphenyl]benzotriazole,

2-[2'-hydroxy-4'-(1"-propylhexyl)oxyphenyl]benzotriazole, 2,2'-methylenebis[4-(1,1,3,3-tetramethylbutyl)-6-(2H-benzotriazole-2-yl)]phenol and a condensate of polyethylene glycol and methyl-3-[3-*t*-butyl-5-(2H-benzotriazole-2-yl)-4-hydroxyphenyl]propionate;

cyanoacrylate based ultraviolet radiation absorbents, such as 2'-ethylhexyl-2-cyano-3,3-diphenylacrylate and the ethyl-2-cyano-3,3-diphenyl acrylate; and

hindered amine based ultraviolet radiation absorbents, such as bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate, succinic acid-bis(2,2,6,6-tetramethyl-4-piperidyl) ester and 2-(3,5-di-*t*-butyl) malonate-bis(1,2,2,6,6-pentamethyl-4-piperidyl) ester; and

1,8-dihydroxy-2-acetyl-3-methyl-6-methoxy naphthalene.

[0055] Examples for the fluorescent dye include 4,4'-bis[2-anilino-4-(2-hydroxyethyl)amino-1,3,5-triazinyl-6-amino]stilbene-2,2'-disulfonic acid disodium salt, 4,4'-bis[2-anilino-4-bis(hydroxyethyl)amino-1,3,5-triazinyl-6-amino]stilbene-2,2'-disulfonic acid disodium salt,

4,4'-bis[2-methoxy-4-(2-hydroxyethyl)amino-1,3,5-triazinyl-6-amino]stilbene-2,2'-disulfonic acid disodium salt,

4,4'-bis[2-methoxy-4-(2-hydroxypropyl)amino-1,3,5-triazinyl-6-amino]stilbene-2,2'-disulfonic acid disodium salt,
 4,4'-bis[2-m-sulfoanilino-4-bis(hydroxyethyl)amino-1,3,5-triazinyl-6-amino]stilbene-2,2'-disulfonic acid disodium salt,
 4-[2-p-sulfoanilino-4-bis(hydroxyethyl)amino-1,3,5-triazinyl-6-amino]-4'-[2-m-sulfoanilino-4-bis(hydroxyethyl)amino-
 1,3,5-triazinyl-6-amino]stilbene-2,2'-disulfonic acid tetrasodium salt, 4,4'-bis[2-p-sulfoanilino-4-bis(hydroxyethyl)ami-
 5 no-1,3,5-triazinyl-6-amino]stilbene-2,2'-disulfonic acid tetrasodium salt,
 4,4'-bis[2-(2,5-disulfoanilino)-4-phenoxyamino-1,3,5-triazinyl-6-amino]stilbene-2,2'-disulfonic acid hexasodium salt,
 4,4'-bis[2-(2,5-disulfoanilino)-4-(p-methoxycarbonylphenoxy)amino-1,3,5-triazinyl-6-amino]stilbene-2,2'-disulfonic ac-
 id hexasodium salt, 4,4'-bis[2-(p-sulfophenoxy)-4-bis(hydroxyethyl)amino-1,3,5-triazinyl-6-amino]stilbene-2,2'-disul-
 fonic acid tetrasodium salt,
 10 4,4'-bis[2-(2,5-disulfoanilino)-4-formalinylamino-1,3,5-triazinyl-6-amino]stilbene-2,2'-disulfonic acid hexasodium acid
 and
 4,4'-bis[2-(2,5-disulfoanilino)-4-bis(hydroxyethyl)amino-1,3,5-triazinyl-6-amino]stilbene-2,2'-disulfonic acid hexaso-
 dium salt.

[0056] Different kinds of material used for making each element of the color forming dye have been explained. The
 15 elements include the developer, the image stabilizer, the sensitizer, the filler, the dispersing agent, the antioxidant, the
 desensitizer, the antitack agent, the antifoamer, the photostabilizing agent and the fluorescent dye. In making each of
 the elements, every kind of material can be utilized alone without mixing with others. As an alternative, each kind of
 material can be utilized by mixing with any of the other kinds. The ratio of each element to be used with respect to a
 color forming dye is 0.1 to 15 parts by weight based on 1 part by weight of a color forming dye, and preferably 1 to 10
 20 parts by weight.

[0057] The recording sheet provided by the present invention has a recording material layer created on a base sheet
 from a recording material provided by the present invention. The base sheet can be a paper base sheet, a synthetic
 resin film or a synthetic resin sheet. Examples for the paper base sheet include thin leaf paper, craft paper, titanium
 paper, linter paper, board paper, wood free paper, coated paper, art paper, vegetable paper, glassine paper, parchment
 25 paper, paraffine paper and recycled paper. Examples for the synthetic resin film or the synthetic resin sheet include
 the polyethylene, the polypropylene, the polyvinyl chloride, the polyvinylidene chloride, the ethylene-vinyl acetate co-
 polymer, the ethylene - vinyl alcohol inter polymer, the polyethylene terephthalate, the polybutylene terephthalate, the
 polyethylene naphththalate, the polymethyl methacrylate, the polymethyl acrylate, the polyethyl methacrylate, the pol-
 ystyrene, the cellulose triacetate, the cellophane and the polycarbonate. In particular, use of paper base sheets is
 30 desirable. There are no particular limitations on the thickness of the base sheet. However, the thickness of the base
 sheet normally has a value in the range 1 to 500 micrometers

[0058] Typically, the recording material layer is created by coating the base sheet with a solution or a dispersion of
 the recording material by adoption of a commonly known coating method. The amount of coating is dependent on the
 concentration of the solution or the dispersion liquid. However, it is 0.1 to 100 g/m², desirably 1 to 20 g/m² by dry weight.

[0059] Typical methods of coating the basic sheet with a solution or a dispersion of the recording material provided
 35 by the present invention include, but not limited to, a roll coat method, a curtain flow coat method, a Mayer bar coat
 method, a reversed coat method, a photogravure coat method, a photogravure reversed coat method, an air knife coat
 method, a kiss coat method, a blade coat method, a smooth coat method and a roll knife coat method

[0060] In addition, the recording material layer may be created directly on the base sheet. As an alternative, the
 40 recording material layer may be created above the base sheet, with another layer such as an anchor coat layer sand-
 wiched between the recording material layer and the base sheet. A protection layer may further be created on the
 recording material layer. The anchor coat layer and the protection layer may each be made from a solution or a dis-
 persion, including one or several kinds of commonly known synthetic resin. If necessary, the solution or the dispersion
 may include the other aforementioned elements of the developer, the stabilizer, the sensitizer, the filler, the dispersing
 45 agent, the antioxidant, the desensitizer, the antitack agent, the
 antifoamer, the photo stabilizer and the fluorescent dye.

[0061] In particular, it is desirable to use thermal recording paper and pressure-sensitive copying paper as a material
 for making the recording sheet of the present invention. The thermal recording paper can be manufactured by preparing
 a dispersion, coating the upper surface of the base sheet with the dispersion and, then, drying the base sheet and the
 50 dispersion. The dispersion is prepared by dissolving, for example, fine particles of the color forming dye and fine par-
 ticles of the recording material into an aqueous solution of an aqueous binding agent, such as polyvinyl alcohol and
 the cellulose.

[0062] The pressure-sensitive copying paper can be manufactured by combining a color forming dye sheet and a
 developer sheet. The color forming dye sheet is made by coating the upper surface of a first paper base sheet with a
 55 color forming dye dispersion, which is prepared typically by dispersing microcapsules of a color forming dye by adoption
 of a commonly known method using a proper dispersion. On the other hand, the developer sheet is made by coating
 the upper surface of a second paper base sheet with the dispersion of a developer. During these processes, the re-
 cording material provided by the present invention is dispersed into the color forming dye dispersion or the dispersion

of the developer, or both the dispersions.

[0063] The pressure-sensitive copying paper can also be manufactured as a unit comprising an upper sheet of paper and a lower sheet of paper. The lower surface of the upper sheet of paper is coated with microcapsules, each including the organic solvent solution of the color forming dye and being retained on the surface. The microcapsules also serve as a support material. The upper surface of the lower sheet of paper is coated with the developer (an acidic substance), which also is retained on the surface. As another alternative, the pressure-sensitive copying paper is manufactured as a piece of self content paper. One face of the self content paper is coated with both the developer and microcapsules each including the organic solvent solution of the color forming dye. As the developer for the pressure-sensitive copying paper, developers including, but not limited to, any of the aforementioned typical developers for the pressure-sensitive paper can be used.

Best Modes for Carrying Out the Invention

[0064] Preferred embodiments of the present invention are described in detail as follows. However, the scope of the present invention is not limited to these embodiments. It is to be noted that, unless otherwise specified, the technical term 'unit' used in the following description means a 'weight unit'. A image density (Macbeth value) and a background density (Macbeth value) have been measured by using a Macbeth reflection densitometer manufactured by Macbeth Corporation with a model number of RD-514 and filter number #106.

Synthesis Example 1

Synthesis of N-(4'-hydroxyphenylthio)acetyl-2-hydroxyaniline

[0065] 109.1 g (1 mol) of 2-aminophenol, 84.1 g (1 mol) of sodium bicarbonate, 900 mL of acetonitrile and 100 mL of water were added under room temperature into a 2L flask with four inlets and attached with a stirrer and a thermometer. The internal temperature was cool down to 10°C and 112.9 g (1 mol) of chloroacetyl chloride was added to the solution over a period of 3 hours and stirred for 3 hours at room temperature. Following to the completion of the reaction, 10 mL of methanol was added, and then acetonitrile was distilled out under reduced pressure and the resultant residue was subjected to recrystallization with toluene. Then, salt was taken out in a cleaning process using water to obtain 2-chloroacetyl-2-hydroxyaniline.

[0066] Then, 126.2 g (1 mol) of 4-mercaptophenol, 66 g (1 mol) of potassium hydroxide and 1 L of methanol were added under room temperature into a 3L flask with four inlets and attached with a stirrer and a thermometer. After confirming that potassium hydroxide added is completely dissolved, temperature inside the resultant solution was cool down to 10°C, then 2-chloroacetyl-2-hydroxyaniline obtained as a result of the reaction described above was added to the solution and stirred at room temperature for 3 hours. Following to the completion of the reaction, 2 L of water was added and separated crystals was filtered to give 210 g of N-(4'-hydroxyphenylthio)acetyl-2-hydroxyaniline. The yield was 76% and the melting point was in a range of 176 to 179°C.

Synthesis Example 2

Synthesis of N-(4'-hydroxyphenylthio)acetyl-4-hydroxyaniline

[0067] Synthesis example 2 was obtained according to the same process as described in the synthesis example 1, except that, 4-aminophenol is replaced by 2-aminophenol. The melting point was in a range 163 to 164°C.

Synthesis Example 3

Synthesis of N-(4'-hydroxyphenylthio)acetyl-3-hydroxyaniline

[0068] Synthesis example 3 was obtained according to the same process as described in the synthesis example 1, except that, 3-aminophenol is replaced by 2-aminophenol. The melting point was in a range 171 to 173°C.

[0069] In addition to synthesis examples 1 to 3 described above, as a method of mixing compositions provided by the present invention, it is possible to adopt other methods such as a method of making reactions using the hydroxy aniline compounds each as a raw material as is the case with the following synthesis examples.

Synthesis Example 4

Synthesis of N-(4'-hydroxyphenylthio)acetyl-2-hydroxyaniline and

5 N-(4'-hydroxyphenylthio)acetyl-4-hydroxyaniline (mixing ratio of 1 : 1)

[0070] 54.6 g (0.5 mol) of 2-aminophenol, 54.6 g (0.5 mol) of 4-aminophenol, 84.1 g (1 mol) of sodium bicarbonate, 900 mL of acetonitrile and 100 mL of water were added under room temperature into a 2L flask with four inlets and attached with a stirrer and a thermometer. The internal temperature was cool down to 10°C and 112.9 g (1 mol) of chloroacetyl chloride was added to the solution over a period of 3 hours and stirred for 3 hours at room temperature.

10 Following to the completion of the reaction, 10 mL of methanol was added, and then acetonitrile was distilled out under reduced pressure and the resultant residue was subjected to recrystallization with toluene. Then, salt was taken out in a cleaning process using water to obtain a mixture of 2-chloroacetyl-2-hydroxyaniline and 2-chloroacetyl-4-hydroxyaniline.

15 [0071] Then, 126.2 g (1 mol) of 4-mercaptophenol, 66 g (1 mol) of potassium hydroxide and 1 L of methanol were added under room temperature into a 3L flask with four inlets and attached with a stirrer and a thermometer. After confirming that potassium hydroxide added is completely dissolved, temperature inside the resultant solution was cool down to 10°C, then a mixture of 2-chloroacetyl-2-hydroxyaniline and 2-chloroacetyl-4-hydroxyaniline obtained as a result of the reaction described above was added to the solution and stirred at room temperature for 3 hours. Following

20 to the completion of the reaction, 2 L of water was added and separated crystals were filtered to give 231 g of a mixture of N-(4'-hydroxyphenylthio)acetyl-2-hydroxyaniline and N-(4'-hydroxyphenylthio)acetyl-4-hydroxyaniline (a mixing ratio of about 50% : 50%). The yield was 80% and the melting point was in a range of 147 to 153°C.

25 First Embodiment (Preparation of the Thermal Recording Paper)

[0072] First of all, dispersion (liquids A to D) including components described below were prepared. It is to be noted that the components have each been well ground by using a sand grinder.

30 • Dye Dispersion (Liquid A)

The dye dispersion referred to as liquid A is a liquid obtained as a result of dispersing 3-di-n-butylamino-6-methyl-7-anilinoftuoran with a weight of 16 units in 84units of an aqueous solution containing 10% polyvinyl alcohol.

35 • Developer Dispersion (Liquid B)

The developer dispersion referred to as liquid B is a liquid obtained as a result of dispersing N-(4'-hydroxyphenylthio)acetyl-2-hydroxyaniline with a weight of 8 units and N-(4'-hydroxyphenylthio)acetyl-4-hydroxyaniline with a weight of 8 units in 84units of an aqueous solution containing 10% polyvinyl alcohol.

40 • Sensitizer Dispersion (Liquid C)

The sensitizer dispersion referred to as liquid C is a liquid obtained as a result of dispersing di(4-methylbenzyl) oxalate with a weight of 16 in 84units of an aqueous solution containing 10% polyvinyl alcohol.

• Filler Dispersion (Liquid D)

45 The filler dispersion liquid referred to as liquid D is a liquid obtained as a result of dispersing calcium carbonate with a weight of 27.8 units in 26.2 units of an aqueous solution containing 10% polyvinyl alcohol and water with a weight of 71 units.

[0073] These dispersions were mixed at weight proportions of liquid A : liquid B : liquid C : liquid D set at 1 : 2 : 1 : 4 in order to prepare a coating liquid of a recording material for the thermal recording paper.

50 [0074] Then, the surface of a piece of base paper was coated with 5.5 g/m² (dry weight) of the coating liquid of the recording material by using a wire rod manufactured by Wave Star Corporation with a commodity name of Wire Bar and a commodity number of 12. After a drying process, a calendaring process was carried out to make the thermal recording paper. Visual observation of the produced thermal recording paper confirmed that there is no background fogging.

55

Second Embodiment

[0075] In accordance with a second embodiment, a recording material was prepared in order to manufacture the thermal recording paper by adoption of the same method as the first embodiment except that liquid E described below was used as a substitute for the developer dispersion referred to as liquid B.

Developer Dispersion (Liquid E)

[0076] A developer dispersion referred to as liquid E is a liquid obtained as a result of dispersing N-(4'-hydroxyphenylthio)acetyl-2-hydroxyaniline with a weight of 8 units and N-(4'-hydroxyphenylthio)acetyl-3-hydroxyaniline with a weight of 8 units in 84units of an aqueous solution containing 10% polyvinyl alcohol. Visual observation of the produced thermal recording paper confirmed that there is no background fogging.

Third Embodiment

[0077] In accordance with a third embodiment, a recording material was prepared in order to manufacture the thermal recording paper by adoption of the same method as the first embodiment except that liquid F described below was used as a substitute for the developer dispersion liquid referred to as liquid B.

Developer Dispersion (Liquid F)

[0078] A developer dispersion referred to as liquid F is a liquid obtained as a result of dispersing N-(4'-hydroxyphenylthio)acetyl-2-hydroxyaniline with a weight of 5.3 units, N-(4'-hydroxyphenylthio)acetyl-3-hydroxyaniline with a weight of 5.3 units and N-(4'-hydroxyphenylthio)acetyl-4-hydroxyaniline with a weight of 5.3 units in 84units of an aqueous solution containing 10% polyvinyl alcohol. [0079] Visual observation of the produced thermal recording paper confirmed that there is no background fogging.

Comparison Example 1

[0080] In accordance with comparison example 1, a recording material was prepared in order to manufacture the thermal recording paper by adoption of the same method as the first embodiment except that liquid K described below was used as a substitute for the developer dispersion referred to as liquid B.

Developer Dispersion (Liquid K)

[0081] A developer dispersion referred to as liquid K is a liquid obtained as a result of dispersing 2,4'-dihydroxydiphenylsulfone with a weight of 16 units in 84units of an aqueous solution containing 10% polyvinyl alcohol.

Comparison Example 2

[0082] In accordance with comparison example 2, a recording material was prepared in order to manufacture the thermal recording paper by adoption of the same method as the first embodiment except that liquid L described below was used as a substitute for the developer dispersion referred to as liquid B.

Developer Dispersion (Liquid L)

[0083] A developer dispersion referred to as liquid L is a liquid obtained as a result of dispersing N-(4'-hydroxyphenylthio)acetyl-2-hydroxyaniline with a weight of 16 units in 84 units of an aqueous solution containing 10% polyvinyl alcohol.

Experiment Example 1 (Measurement of Dynamic Sensitivities)

[0084] A portion of every piece of thermal recording paper made in accordance with each of the first to third embodiments as well as each of comparison examples 1 and 2 was cut out and used as an experiment paper specimen. For each experiment paper specimen, a coloring instrument for dynamic sensitivity was used. The apparatus was manufactured by Ohkura Electric Corporation (model number TH - PMD). Subsequently, heat energy was added under conditions of 0.38 and 0.50 m J per dot. Then, image density (Macbeth values) of the experiment paper specimens were measured to give results of measurement as shown in the first table. As is obvious from the first table, the pieces

of thermal recording paper, which were made in accordance with the first to third embodiments, are known to each have a high dynamic sensitivity of the same order as the pieces of thermal recording paper, which were made in accordance with comparison examples 1 and 2.

5 Experiment Example 2 (Heat & Humidity resistance tests of image)

[0085] A portion of every piece of thermal recording paper made in accordance with each of the first to third embodiments as well as each of comparison examples 1 and 2 was cut out and used as an experiment paper specimen. Subsequently, heat energy was added to get the state of saturated density of image. Each of the experiment paper specimens in the state of saturated colored was then kept for 24 hours at a temperature of 50°C and a humidity of 80% in a incubator controlled humidity and temperature manufactured by Futaba Science Corporation (model number GL-42). Right after the state of saturated colored and keeping after 24-hour in the incubator controlled humidity and temperature, image density (Macbeth values) of the experiment paper specimens were measured to give results of measurement as shown in the first table. As is obvious from the first table, the pieces of thermal recording paper, which were made in accordance with the first to third embodiments, are known to each have heat and humidity resistance superior to the pieces of thermal recording paper, which were made in accordance with comparison examples 1 and 2.

Experiment Example 3 (Heat resistance tests of image)

[0086] A portion of every piece of thermally sensitive recording paper made in accordance with each of the first to third embodiments as well as each of comparison examples 1 and 2 was cut out and used as an experiment paper specimen. Subsequently, heat energy was added to get the state of saturated density of image in the same way as experiment example 1. Each of the experiment paper specimens in the state of saturated colored was then kept for 24 hours at a temperature of 90°C in a constant temperature oven manufactured by Yamato Science Corporation (model number DK - 400). Right after the state of saturated colored and keeping after the 24 - hour in the constant temperature oven, image density (Macbeth values) of the experiment paper specimens were measured to give results of measurement as shown in the first table. As is obvious from the first table, the pieces of thermal recording paper, which were made in accordance with the first to third embodiments, are known to each have a heat resistance superior to the pieces of thermal recording paper, which were made in accordance with comparison examples 1 and 2.

Experiment Example 4 (Light resistance tests of image)

[0087] A portion of every piece of thermal recording paper made in accordance with each of the first to third embodiments as well as each of comparison examples 1 and 2 was cut out and used as an experiment paper specimen. Subsequently, heat energy was added to get the state of saturated density of image in the same way as experiment example 1. Then, after an ultraviolet ray beam having a wavelength of 380 nm was radiated to each of the experiment paper specimens for 24 hours or 72 hours by using a UV auto-fade-meter equipped with an Ultraviolet Carbon Arc lamp manufactured by Suga Testing Equipment Corporation with a commodity name of ultraviolet long-life fade meter and a model number of FAL - 5, image density (Macbeth values) of the experiment paper specimens were measured to give measurement results and remaining rates(residual) summarized as shown in the first table. A remaining rate (residual) expressed in terms of percents is defined as a ratio of the post-experiment image density to a pre-experiment image density. As is obvious from the first table, the pieces of thermal recording paper, which were made in accordance with the first to third embodiments, are known to each have a light resistance of the same order as the pieces of thermal recording paper, which were made in accordance with comparison examples 1 and 2.

Experiment Example 5 (Plasticizer resistance tests of image part- I)

[0088] A portion of every piece of thermal recording paper made in accordance with each of the first to third embodiments as well as each of comparison examples 1 and 2 was cut out and used as an experiment paper specimen. Subsequently, heat energy was added to get the state of saturated density of image. Then, a vinyl-chloride wrap film including a plasticizer was stuck on to the color-developing surface of each of the experiment paper specimens. The experiment paper specimens were then kept in this state for eight hours at a temperature of 25°C.

[0089] Right after the state of saturated color development and after the eight-hour storage period at the temperature of 25°C, image density (Macbeth values) of the experiment paper specimens were measured to give results of measurement as shown in the first table. As is obvious from the first table, the pieces of thermal recording paper, which were made in accordance with the first to third embodiments, are known to each have a plasticizer resistance superior to the pieces of thermal recording paper, which were made in accordance with comparison examples 1 and 2.

Experiment Example 6 (Water resistance tests of image part- I)

[0090] A portion of every piece of thermal recording paper made in accordance with each of the first to third embodiments as well as each of comparison examples 1 and 2 was cut out and used as an experiment paper specimen. Subsequently, heat energy was added to get the state of saturated density of image in the same way as experiment example 1. Then, each of the experiment paper specimens was submerged in pure water at a temperature of 25°C for seven days. Right after the state of saturated colored and after the seven-day submersion period at a temperature of 25°C, image density (Macbeth values) of the experiment paper specimens were measured to give results of measurement as shown in the first table. As is obvious from the first table, the pieces of thermal recording paper, which were made in accordance with the first to third embodiments, are known to each have a water resistance superior to the pieces of thermal recording paper, which were made in accordance with comparison examples 1 and 2. The results of experiment examples 1 to 6 prove that the thermal recording paper provided by the present invention has an excellent dynamic sensitivity as well as a heat and humidity resistance, a heat resistance, a light resistance, a plasticizer resistance and a water resistance, which are all also excellent as well.

for the sensitizer or dye of the thermal recording paper made in accordance with the first embodiment of the present invention.

Fourth Embodiment

[0092] In accordance with a fourth embodiment, a recording material was prepared in order to manufacture the thermal recording paper by adoption of the same method as the first embodiment except that liquid G described below was used as a substitute for the sensitizer dispersion referred to as liquid C.

Sensitizer Dispersion (Liquid G)

[0093] A sensitizer dispersion referred to as liquid G is a liquid obtained as a result of dispersing 1,2-bis(phenoxy) ethane with a weight of 16 units in 84units of an aqueous solution containing 10% polyvinyl alcohol. Visual observation of the produced thermal recording paper confirmed that there is no background fogging.

Fifth Embodiment

[0094] In accordance with a fifth embodiment, a recording material was prepared in order to manufacture the thermal recording paper by adoption of the same method as the first embodiment except that liquid H described below was used as a substitute for the sensitizer dispersion referred to as liquid C.

Sensitizer Dispersion (Liquid H)

[0095] A sensitizer dispersion liquid referred to as liquid H is a liquid obtained as a result of dispersing diphenylsulfone with a weight of 16 units in 84units of an aqueous solution containing 10% polyvinyl alcohol. Visual observation of the produced thermal recording paper confirmed that there is no background fogging.

Sixth Embodiment

[0096] In accordance with a sixth embodiment, a recording material was prepared in order to manufacture the thermal recording paper by adoption of the same method as the first embodiment except that liquid I described below was used as a substitute for the dye dispersion dispersion to as liquid A.

Dye Dispersion (Liquid I)

[0097] A dye dispersion referred to as liquid I is a liquid obtained as a result of dispersing 3-(N-methyl-N-propylamino)-6-methyl-7-anilino-fluoran with a weight of 16 units in 84units of an aqueous solution containing 10% polyvinyl alcohol. Visual observation of the produced thermal recording paper confirmed that there is no background fogging..

Seventh Embodiment

[0098] In accordance with a seventh embodiment, a recording material was prepared in order to manufacture the thermal recording paper by adoption of the same method as the first embodiment except that liquid J described below was used as a substitute for the dye dispersion dispersion to as liquid A.

Dye Dispersion (Liquid J)

[0099] A dye dispersion referred to as liquid J is a liquid obtained as a result of dispersing 3-(N-cyclohexyl-N-methylamino)-6-methyl-7-anilino-fluoran with a weight of 16 units in 84units of an aqueous solution containing 10% polyvinyl alcohol. Visual observation of the produced thermal recording paper confirmed that there is no background fogging..

Experiment Example 7 (Heat resistance tests of background)

[0100] A portion of every piece of thermal recording paper made in accordance with each of the first, fourth and fifth embodiments was cut out and used as an experiment paper specimen. Subsequently, each of the experiment paper specimens was put in a Constant Temperature oven at temperatures of 90°C and 100°C for 24 hours. The Constant Temperature oven was manufactured by Yamato Corporation (model

number DK - 400).

[0101] After each of the experiment paper specimens was put in a Constant Temperature oven for 24 hours, background density (Macbeth values) of the experiment paper specimens were measured to give results of measurement as shown in the second table. As is obvious from the second table, by selecting a proper sensitizer, it is known that the heat resistance of background, which are about equal to each other at the temperature of 90°C, can be further improved at the temperature of 100°C.

Table 2

(Results of heat resistance tests of background)		
	Background density after heat resistance tests	
	Macbeth value (90°C)	Macbeth value (100°C)
First embodiment	0.11	0.26
Fourth embodiment	0.10	0.15
Fifth embodiment	0.11	0.17

Experiment Example 8 (plasticizer resistance tests of image part- II)

[0102] A portion of every piece of thermal recording paper made in accordance with each of the first, sixth and seventh embodiments was cut out and used as an experiment paper specimen. Subsequently, heat energy was added to get the state of saturated density of image in the same way as experiment example 1. Then, a vinyl-chloride wrap film including a plasticizer was stuck to the color-developing surface of each of the experiment paper specimens. The experiment paper specimens were then kept in this state for eight hours at a temperature of 25°C.

Right after the state of saturated colored and keeping after the eight-hour at 25°C, image density (Macbeth values) of the experiment paper specimens were measured to give results of measurement as shown in the third table. As is obvious from the third table, by selecting a proper dye, it is known that plasticizer resistance of image can be further improved.

Experiment Example 9 (Water resistance tests of image part- II)

[0103] A portion of every piece of thermal recording paper made in accordance with each of the first, sixth and seventh embodiments and used as an experiment paper specimen. Subsequently, heat energy was added to get the state of saturated density of image in the same way as experiment example 1. Then, each of the experiment paper specimens was submerged in pure water at a temperature of 25°C for seven days. Right after the state of saturated colored and after the seven-day submersion period at the temperature of 25°C, image density (Macbeth values) of the experiment paper specimens were measured to give results of measurement as shown in the third table. As is obvious from the third table, by selecting a proper dye, it is known that the water resistance of image can be further improved.

Table 3

(Results of plasticizer resistance tests-part II and water resistance tests-part II)					
	Original	Image density after plasticizer resistance test		Image density after water resistance test	
	Macbeth value	Macbeth value	Residual (%)	Macbeth value	Residual (%)
First embodiment	1.17	0.39	33	0.85	73
Reference example 3	1.18	0.65	55	1.09	92
Reference example 4	1.20	0.74	62	0.94	78
• Residual expressed in terms of percents is defined as a ratio of the post-experiment image density to a pre-experiment image density.					

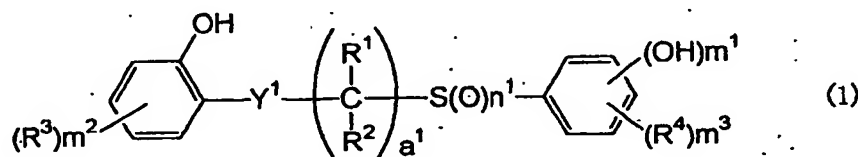
INDUSTRIAL APPLICATION POSSIBILITY

[0104] As described above, in accordance with the present invention, it is possible to provide a recording material and a recording sheet that cause no background fogging phenomenon and have an excellent dynamic sensitivity as well as an excellent image stability, particularly, such as a heat and humidity resistance, a heat resistance, a light resistance, a plasticizer resistance and a water resistance. In addition, it is possible to provide a recording material and a recording sheet wherein, if necessary, by selecting a sensitizer in applications of the recording material and the recording sheet, their heat resistance of background can be improved and, by selecting a proper dye in applications of the recording material and the recording sheet, their plasticizer resistance of image as well as their water resistance of image can be improved.

Claims

1. A composition including:

at least one type of a compound represented by Formula (1); wherein



R¹ and R² each independently represent hydrogen or C1 - C6 alkyl,

a¹ represents an integer of 1 to 6,

n¹ represents 0, 1 or 2,

m¹ represents 0 or an integer in the range 1 to 3,

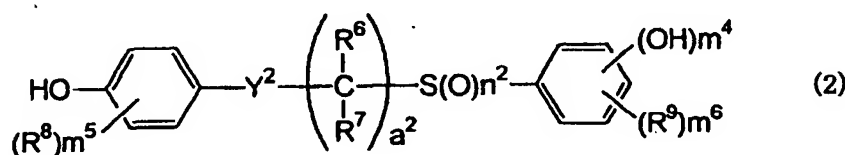
R³ and R⁴ each independently represent nitro, carboxyl, halogen, C1-C6 alkyl or C2-C6 alkenyl,

m² and m³ each independently represent 0, 1 or 2;

R³ and R⁴ may be different to each other when m² and m³ represent each 2,

Y¹ represents CO or NR⁵CO (in the equation, R⁵ represents hydrogen or C1-C6 alkyl);

at least one type of a compound represented by Formula (2); wherein



R⁶ and R⁷ each independently represent hydrogen or C1 - C6 alkyl,

a² represents an integer of 1 to 6,

n² represents 0, 1 or 2,

m⁴ represents 0 or an integer in the range 1 to 3,

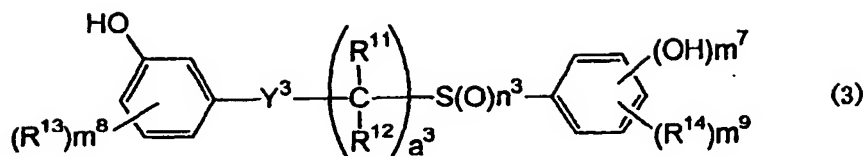
R⁸ and R⁹ each independently represent nitro, carboxyl, halogen, C1-C6 alkyl or C2-C6 alkenyl,

m⁵ and m⁶ each independently represent 0, 1 or 2;

R⁸ and R⁹ may be different to each other when m⁵ and m⁶ represent each 2,

Y² represents CO or NR¹⁰CO (in the equation, R¹⁰ represents hydrogen or C1-C6 alkyl); and/or

at least one type of a compound represented by Formula (3); wherein



R¹¹ and R¹² each independently represent hydrogen or C1 - C6 alkyl,

a³ represents an integer of 1 to 6,

n³ represents 0, 1 or 2,

m⁷ represents 0 or an integer in the range 1 to 3,

R¹³ and R¹⁴ each independently represent nitro, carboxyl, halogen, C1-C6 alkyl or C2-C6 alkenyl,

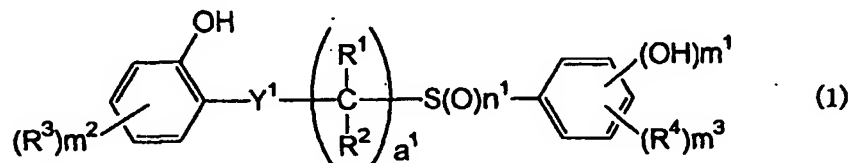
m⁸ and m⁹ each independently represent 0, 1 or 2;

R¹³ and R¹⁴ may be different to each other when m⁸ and m⁹ represent each 2,

Y³ represents CO or NR¹⁵CO (in the equation, R¹⁵ represents hydrogen or C1-C6 alkyl);

2. A recording material comprising:

at least one type of a compound represented by Formula (1) ; wherein



R¹ and R² each independently represent hydrogen or C1 - C6 alkyl,

a¹ represents an integer of 1 to 6,

n¹ represents 0, 1 or 2,

m¹ represents 0 or an integer in the range 1 to 3,

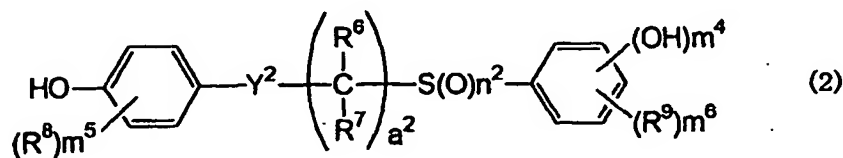
R³ and R⁴ each independently represent nitro, carboxyl, halogen, C1-C6 alkyl or C2-C6 alkenyl,

m² and m³ each independently represent 0, 1 or 2;

R³ and R⁴ may be different to each other when m² and m³ represent each 2,

Y¹ represents CO or NR⁵CO (in the equation, R⁵ represents hydrogen or C1-C6 alkyl) ;

at least one type of a compound represented by Formula (2) ; wherein



R⁶ and R⁷ each independently represent hydrogen or C1 - C6 alkyl,

a² represents an integer of 1 to 6,

n² represents 0, 1 or 2,

m⁴ represents 0 or an integer in the range 1 to 3,

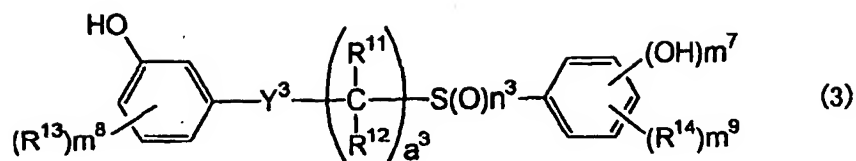
R⁸ and R⁹ each independently represent nitro, carboxyl, halogen, C1-C6 alkyl or C2-C6 alkenyl,

m⁵ and m⁶ each independently represent 0, 1 or 2;

R⁸ and R⁹ may be different to each other when m⁵ and m⁶ represent each 2,

Y² represents CO or NR¹⁰CO (in the equation, R¹⁰ represents hydrogen or C1-C6 alkyl) ; and/or

at least one type of a compound represented by Formula (3) ; wherein



10 R¹¹ and R¹² each independently represent hydrogen or C1 - C6 alkyl,

a³ represents 0, 1 or 2,

n³ represents an integer of 0 to 2,

m⁷ represents 0 or an integer in the range 1 to 3,

15 R¹³ and R¹⁴ each independently represent nitro, carboxyl, halogen, C1-C6 alkyl or C2-C6 alkenyl,

m⁸ and m⁹ each independently represent 0, 1 or 2;

R¹³ and R¹⁴ may be different to each other when m⁸ and m⁹ represent each 2,

Y³ represents CO or NR¹⁵CO (in the equation, R¹⁵ represents hydrogen or C1-C6 alkyl);

- 20 3. A recording material according to claim 2 wherein the compound represented by Formula (2) according to claim 2 and/or the compound represented by Formula (3) according to claim 2 each have a content quantity in the range 5 to 500 parts by weight relative to 100 parts by weight of the compound represented by Formula (1) according to claim 2.

- 25 4. A recording sheet comprising a base sheet and a recording material layer made from a recording material according to claim 2 or 3 on the said base sheet.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP02/03159

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl ⁷ B41M5/30, C08J7/04 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int.Cl ⁷ B41M5/30, C08J7/04 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1922-1996 Toroku Jitsuyo Shinan Koho 1994-2002 Kokai Jitsuyo Shinan Koho 1971-2002 Jitsuyo Shinan Toroku Koho 1996-2002 Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) REGISTRY (STN), CA (STN)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	WO 01/25193 A1 (Nippon Soda Co., Ltd.), 12 April, 2001 (12.04.01), Full text & AU 200075555 A	1-4
X	JP 63-153182 A (Fuji Photo Film Co., Ltd.), 25 June, 1988 (25.06.88), Full text (Family: none)	1-4
A	JP 3-293195 A (Mitsubishi Paper Mills Ltd.), 24 December, 1991 (24.12.91), Full text (Family: none)	1-4
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "Z" document member of the same patent family		
Date of the actual completion of the international search 20 June, 2002 (20.06.02)		Date of mailing of the international search report 02 July, 2002 (02.07.02)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.		Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 1998)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP02/03159

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2-293195 A (Ricoh Co., Ltd.), 14 August, 1990 (14.08.90), Full text (Family: none)	1-4
X	US 4075227 A (Eli Lilly and Co.), 21 February, 1978 (21.02.78), Full text (Family: none)	1
P,A	JP 2001-288163 A (Nippon Soda Co., Ltd.), 16 October, 2001 (16.10.01), Claims (Family: none)	1-4

Form PCT/ISA/210 (continuation of second sheet) (July 1998)